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(54) Title: TOUGH POLY(META-XYLYLENE ADIPAMIDE) WITH HIGH FLEXURAL MODULUS (57) Abstract A blend of 50-90 % of poly(m-xylylene adipamide) with 5-25 % of EPDM rubber grafted with maleic anhydride and 5-25 % of an ethylene/alkyl acrylate or methacrylate/glycidyl acrylate or methacrylate terpolymer has high notched Izod impact strength, high flexural modulus, low moisture sensitivity, and good elongation at break.		

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TITLE

TOUGH POLY (META-XYLYLENE ADIPAMIDE) WITH HIGH FLEXURAL MODULUS

BACKGROUND OF THE INVENTION

5 This invention relates to an improved polyamide composition that is very tough, has low moisture sensitivity, and retains good flexural modulus.

Polyamides are well known industrial polymers, finding numerous applications in such diversified fields as textile fibers, molding
10 resins, films, and composites. The commercially most important polyamide is poly(hexamethylene adipamide), also known as nylon 66; and the next most important commercial polyamide is poly(ϵ -caprolactam), also known as nylon 6. Another, much more recently commercialized polyamide is poly(m-xylylene adipamide), (sometimes referred to herein as poly-MXD6),
15 which is sold by Mitsubishi Gas Chemical Company, Inc. of Japan under the tradename "RENY". While both nylon 66 and nylon 6 can be made very tough by the addition of certain rubbery materials, as described in U.S. Patent 4,174,358 to Epstein, they are somewhat moisture-sensitive and have only a modest flex modulus. Poly(m-xylylene adipamide), however, has a
20 flex modulus that under dry conditions is about 50% higher than that of nylon 66. It also is significantly less sensitive to moisture than nylon 66. Yet, poly-MXD6 has some drawbacks, such as having a very low elongation at break (less than 3%) and being very brittle (notched Izod value of 20-25 J/m). Because of those, poly-MXD6 has achieved only a limited industrial
25 acceptance in the United States. Additives such as, for example, EPDM rubber grafted with maleic anhydride (EPDMG) or ethylene/butyl acrylate/glycidyl methacrylate (E/BA/GMA) terpolymer, increase the toughness of poly-MXD6 when present in amounts of 25 % by weight or less, but the improvement is far from dramatic, and the poly-MXD6 thus
30 toughened still fails in a brittle fashion after impact.

Blending poly-MXD6, after proper solid phasing, with EPDMG can in some cases improve the notched Izod value of the polyamide. Solid phasing is a procedure for increasing the molecular weight of a polyamide by passing an inert gas, such as nitrogen, through a bed of

resin pellets, which is maintained at a temperature between the glass transition temperature and the melt temperature of the polyamide. Proper solid phasing improves the toughness of rubber/poly-MXD6 blends by increasing the melt viscosity of poly-MXD6, thus improving rubber dispersion as a result of a better viscosity match between the rubber and the polyamide. However, a rubber-toughened poly-MXD6 with a consistently attainable notched Izod impact value of over 500 J/m, is desirable since this leads to non-brittle type of failure upon impact. Yet, using solid phasing does not achieve this goal for EPDMG-toughened poly-MXD6. This may be due in part to a significant reduction by solid phasing of amine end group concentration and thus reduced interaction of amine groups with anhydride groups of EPDMG.

Accordingly, there is a need in the art for improving poly-MXD6 by increasing its toughness so that it does not exhibit brittle failure upon impact.

SUMMARY OF THE INVENTION

According to the present invention, there is now provided a toughened poly(m-xylylene adipamide) composition having a flexural modulus of at least 2 MPa, when measured according to ASTM D-790 and a notched impact strength of at least 500 J/m, said composition consisting of a blend of about 50-90% of poly(m-xylylene adipamide) with complementary amounts of 5-25% of EPDM rubber grafted with about 0.2-5% of maleic anhydride or maleic anhydride precursor and about 5-25% of an E/X/Y terpolymer in which E stands for ethylene; X stands for an alkyl acrylate or methacrylate; and Y stands for glycidyl acrylate or glycidyl methacrylate, and the respective monomer percentages are about 40-90%, 10-40%, and 0.5-20%, their sum always being 100%; all the percentages being by weight.

Such blends exhibit a greatly improved notched Izod impact strength, as compared with uncompounded poly-MXD6 and a higher flex modulus than either nylon 66 or nylon 6 toughened to the same degree. Further, those blends retain the low moisture sensitivity of poly-MXD6.

DETAILED DESCRIPTION OF THE INVENTION

Poly-MXD6 is, as earlier indicated, a commercial product manufactured by Mitsubishi Gas Chemical company, Inc. This material may

3

be available in different grades, although the particular grade used in the experiments reported in the examples, below, was designated "RENY" 6001. Quantitative analyses established that this polymer had an amine end group concentration of about 40 equivalents per 10^6 g and a carboxyl group concentration of about 80 equivalents per 10^6 g. The relative viscosity of this polyamide was found to be about 19.

EPDM rubber grafted with maleic anhydride or maleic anhydride precursor can be made according to the process described in U.S. Patent 3,884,882 to Caywood. The term "maleic anhydride precursor" includes other unsaturated compounds capable of being grafted onto EPDM rubber and of being converted under the grafting conditions, at least in part, to maleic anhydride or of forming after grafting a succinic anhydride unit. Typical such precursors include, *i.e.*, maleic acid, fumaric acid, and lower alkyl monoesters of maleic and fumaric acids such as, for example, monoethyl maleate, monomethyl maleate, monoethyl fumarate, and monomethyl fumarate. EPDM rubbers are well known to the art as terpolymers or tetrapolymers of ethylene with one or two ethylenically unsaturated monomers and with a diene having only one terminal double bond.

E/X/Y terpolymers suitable in the present invention also are well known. They can be made by copolymerization of ethylene with the other two monomers under pressure in the presence of a free radical initiator, at elevated temperatures, preferably about 100-270°C, especially 130-230°C, and at elevated pressures, preferably at least 70 MPa, and especially 140-350 MPa. This is most advantageously done in a continuous process, adjusting the monomer ratios according to the final comonomer composition in the terpolymer while taking into account the different respective polymerization activities of the comonomers. The general procedures for making terpolymers of ethylene with ethylenically unsaturated comonomers are well known, for example from U.S. Patents 4,351,931 to Armitage; 3,658,741 to Knutson et al.; and 3,115,485 to Bartl et al. The preferred comonomer weight ratio in the E/X/Y terpolymer is about 55-83:15-35:2-10, especially 57-77:20-35:3-8. Typical such E/X/Y terpolymers include ethylene/*n*-butyl acrylate/glycidyl methacrylate,

ethylene/isobutyl acrylate/glycidyl methacrylate, ethylene/methyl methacrylate/glycidyl methacrylate, and ethylene/methyl methacrylate/glycidyl acrylate terpolymers.

The preferred weight ratio of grafted EPDM rubber to E/X/Y terpolymer is 1:4 to 4:1, especially 1:1 to 2:1. The preferred weight ratio of poly-MXD6 to the sum of grafted EPDM rubber and E/X/Y terpolymer is 1:1 to 9:1, especially 3:1 to 4:1.

Blending of poly-MXD6 with the other two components of the improved compositions of the present invention can be accomplished in a conventional manner in standard equipment, preferably under high shear and at an elevated temperature at which all three polymers are in the melt. Typical such equipment includes single-screw and twin-screw extruders, rubber mills, and Banbury mixers.

The composition of the present invention may be further blended with small amounts of additional components which would not detract from the operability of the invention, such as, for example, additional plastic or elastomeric resins, antioxidants, stabilizers, pigments, plasticizers, and melt processing aids, as is generally known and practiced in the art of compounding polymers.

This invention is now illustrated by the following examples of certain preferred embodiments thereof, where all parts, proportions, and percentages are by weight unless otherwise indicated.

Examples 1-9

Poly-MXD6, "RENY" 6001, was used as received from Mitsubishi Gas Chemical Company, Inc., unless otherwise indicated. In Examples 4 and 5, it first was solid phased in a stream of nitrogen at 190° C for 24 hours. In Example 7, it was first solid phased in a stream of nitrogen at 180° C for 3 hours. EPDMG rubber was a graft of 1.5-2.0% of maleic anhydride on a backbone of an ethylene/propylene/1,4-hexadiene 70:24:6 terpolymer made according to the teachings of U.S. Patent 3,884,882. The E/X/Y terpolymer was a 66.7:28.5:3 ethylene/n-butyl acrylate/glycidyl methacrylate (E/BA/GMA) terpolymer. These polymers were blended for about 30 seconds at 270-290° C melt temperature in a Werner & Pfleiderer twin-screw extruder. In each case, the blend was extruded into pellets and

5

injection molded into test specimens, which were subjected to the standard determination of their mechanical properties as follows: tensile strength, ASTM D-638-58T; elongation at break, ASTM D-638-58T; flex modulus, ASTM D-790-58T; notched Izod impact strength, ASTM D-256-56. All test data not obtained in SI units have been converted to SI units.

The results of these experiments are reported in the following

Table I:

TABLE I

Ex. No.	Composition, %				Mechanical Properties*			
	<u>MXD6</u>	<u>Grafted EPDM</u>	<u>E/BA/GMA Terpoly.</u>	<u>EPDM Rubber</u>	<u>Tensile Strength kPa</u>	<u>Elong. %</u>	<u>Flex Mod. MPa</u>	<u>Notched Izod J/m</u>
1	81	10	--	9	62.0(59.3)	24(34)	2.6(3.1)	213(256)
2	75	25	--	--	51.0	47	2.1	427
3	70	30	--	--	44.8	78	1.7	801
4	75	13	--	12	51.7	12	2.1	278
5	81	10	--	9	58.6	24	2.4	117
6	77	15	8	--	51.7	56(-)	2.2(2.3)	1030(993)
7	81	10	--	9	66.2(61.4)	11(23)	2.6(3.1)	427
8	77	15	8	--	49.6	42	2.1	1025
9	80	--	20	--	68.9	110	2.7	48

* Data in parentheses were obtained at 50% relative humidity

The results of the above Examples 1 and 2 show that using EPDMG alone or a combination of EPDM and EPDMG, with a total combined rubber content of up to 25% of the weight of the blends, the toughened poly-MXD6 still exhibited brittle failure upon impact. While the 30:70 EPDMG:poly-MXD blend of Example 3 did exhibit non-brittle failure upon impact, this was achieved at a significant sacrifice of the unique high flex modulus of the polyamide. By contrast, a typical nylon 6 or nylon 66 will normally exhibit non-brittle failure upon impact in the presence of only 20% of EPDMG or less.

Examples 4 and 5 show that solid phasing poly-MXD6 at 190° C in a stream of nitrogen for 24 hours failed to improve the toughness of the rubber/polyamide blends. This was so in spite of the fact that solid phasing increases poly-MXD6 relative viscosity from about 19 to over 50. Under these conditions, the amine end group concentration is reduced from about 40 to about 10 equivalents per 10^6 g. Example 7 shows that solid phasing poly-MXD6 in a stream of nitrogen at 180° C for 3 hours did improve the toughness of the rubber/poly-MXD6 blends but the mode of impact failure still was brittle.

Examples 6 and 8 show the exceptional improvement of notched Izod impact strength obtained with a combination of grafted EPDM rubber and an E/X/Y terpolymer according to the present invention.

Example 9 shows that a 20:80 blend of E/BA/GMA terpolymer with poly-MXD6 alone, while having good elongation properties, has a very poor notched Izod impact strength.

I CLAIM:

1. Poly(m-xylylene adipamide) composition having a flex modulus of at least 2 MPa, when measured according to ASTM D-790-58T and a notched Izod impact strength of at least 500 J/m, when measured
5 according to ASTM D-256-56, said composition consisting of a blend of about 50-90% of poly(m-xylylene adipamide) with complementary amounts of 5-25% of EPDM rubber grafted with about 0.2-5% of maleic anhydride and about 5-25% of an E/X/Y terpolymer in which E stands for ethylene; X stands for an alkyl acrylate or methacrylate; and Y stands for glycidyl
10 acrylate or glycidyl methacrylate, and the respective monomer percentages are about 40-90%, 10-40%, and 0.5-20%, their sum always being 100%; all the above percentages being by weight.
2. A composition of Claim 1 wherein the E/X/Y terpolymer is an ethylene/n-butyl acrylate/glycidyl methacrylate terpolymer.
- 15 3. A composition of Claim 1 wherein the E/X/Y terpolymer is an ethylene/isobutyl acrylate/glycidyl methacrylate terpolymer.
4. A composition of Claim 1 wherein the E/X/Y terpolymer is an ethylene/methyl methacrylate/glycidyl methacrylate terpolymer.
5. A composition of Claim 1 wherein the respective
20 comonomer percentages in the E/X/Y terpolymer are 55-83:15-35:2-10.
6. A composition of Claim 5 wherein respective comonomer percentages in the E/X/Y terpolymer are 57-77:20-35:3-8.
7. A composition of Claim 1 wherein the ratio of grafted EPDM rubber to E/X/Y terpolymer is 1:4 to 4:1.
- 25 8. A composition of Claim 7 wherein the ratio of grafted EPDM rubber to E/X/Y terpolymer is 1:1 to 2:1.
9. A composition of Claim 8 wherein the weight ratio of poly(meta-xylylene adipamide) to the sum of grafted EPDM rubber and E/X/Y terpolymer is 1:1 to 9:1.
- 30 10. A composition of Claim 9 wherein the weight ratio of poly(meta-xylylene adipamide) to the sum of grafted EPDM rubber and E/X/Y terpolymer is 3:1 to 4:1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/07907

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.C1.5 C 08 L 77/00 C 08 L 77/06 //(C 08 L 77/06 C 08 L 51:06 C 08 L 23:08)		
II. FIELDS SEARCHED		
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Classification System	Classification Symbols	
Int.C1.5	C 08 L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	Data Base Chemical Abstracts (Host STN), vol. 12, no. 112, 19 March 1990, (Columbus, Ohio, US), see abstract no. 100371w, & JP,A,01245054 (NIPPON PETROCHEMICALS) 29 September 1989, see abstract -----	1-10
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IV. CERTIFICATION		
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